# UTILIZATION OF WASTE

UDC 666.112.5:666.11.01

# LOW-MELTING GLASSES BASED ON PHOSPHATE ORE PROCESSING PRODUCTS

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Translated from Steklo i Keramika, No. 5, pp. 3 – 5, May, 2000.

The possibility of producing low-melting glasses using phosphate ore processing products as batch components is investigated. Glasses of various shades of green, yellow, and brown with satisfactory properties are synthesized. The resulting glasses have a unique decorative effect imitating the gem texture.

Under current economic conditions, where the possibilities of operating new deposits are limited and environmental requirements are becoming more stringent, industrial waste and recycled resources contribute to expansion of the material basis of the glass industry. The development of new glasses made of nontraditional materials is motivated by economic aspects (saving of energy, natural resources, and industrial materials) and environmental aspects (decrease in air and environmental pollution). That is why industrial wastes are increasingly used in production of glass and glazes. This industry makes use of mineral rocks and products of their processing, waste from ferrous and nonferrous metallurgical production in the form of ash and slime, and chemical wastes (alkaline-earth metals, technical sodium sulfate, galvanic wastes, etc.)

The purpose of the present study is to develop the optimum compositions for low-melting decorative glasses with a maximum content of phosphate ore processing products.

The possibility of producing glasses based on substandard phosphorite ores from the Ratnovskoe deposit (Volyn Region) and gravitation slime, which is the waste of processing bedrock ore from the Stremigorodskoe deposit (Zhitomir Region), has been studied. Phosphorus-containing substandard rocks represent a loose mixture of sand with 0.16 – 0.08 mm grains, i.e., they correspond to the size of sand grains used in glass melting. The phase composition of the ore is represented by quartz, apatite-like calcium phosphate, aragonite, calcite, and hydromica. Bedrock gravitation slime has the form of a finely dispersed dark-colored mixture. The chemical composition of the considered wastes is given in Table 1.

A low-melting glass developed previously [1] and taken as the basis for the present study had the following chemical composition (mole %): 29.8 $SiO_2$, 18.0 $B_2O_5$, 1.3 $Al_2O_3$, 3.6 $P_2O_5$, 10.0 ZnO, 13.3 CaO, 24.0 $Na_2O$, and the temperature of its synthesis was 1200°C. At first, experimental melting was performed for the purpose of determining the quantity of substandard rock which can be added to the composition of the initial glass without modifying its main physicochemical properties and melting conditions. A series of glass batches was prepared, in which the required quantity of sand (from 50 to 100%) was replaced by rock. In addition to the ore, the batches contained boric acid, soda, and zinc and aluminum oxides. It was established that all glasses at temperature 1200°C were sufficiently melted and clarified, i.e., a

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**TABLE 1**

| Material | Mass content, % | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $P_2O_5$ | $TiO_2$ | $SiO_2$ | $Al_2O_3$ | CaO | MgO | FeO | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $SO_3$ | calcination losses |
| Substandard ore of Ratnovskoe deposit | 15.6 | 0.1 | 52.5 | 1.7 | 20.6 | 0.5 | 1.0 | 0.4 | 0.5 | 0.6 | 2.0 | 4.3 |
| Gravitation slime of Stremigorodskoe deposit bedrock ore | 3.4 | 3.7 | 41.2 | 11.2 | 7.3 | 5.0 | 10.2 | – | 1.1 | 2.4 | 2.1 | 12.4 |



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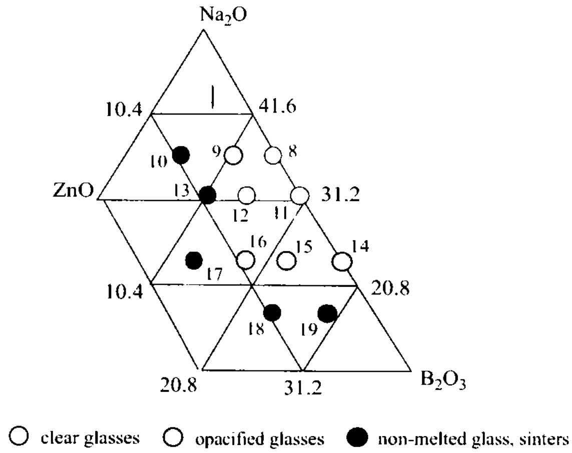


**Fig. 1.** Glass formation in the $SiO_2 - R_2O_3 - P_2O_5 - RO$ $Na_2O$ system; $SiO_2 + P_2O_5 + CaO + R_2O_3 = 48\%$ (molar content).

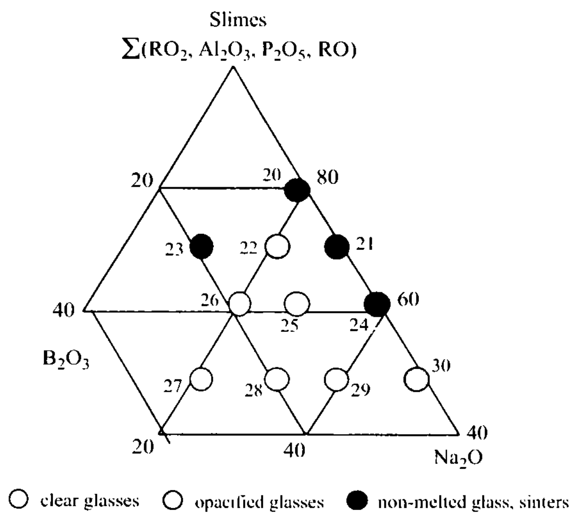


**Fig. 2.** Glass formation in the gravitation slime – $B_2O_3$ – $Na_2O$ system (mass content).

complete replacement of sand, calcium- and phosphorus-bearing materials in the batch by the phosphorite ore wastes was possible (Table 2).

Two series of glasses were synthesized, whose compositions are shown in Figs. 1 and 2.

The content of the introduced ore taken as a constant value or the first series of glasses corresponded to the introduction of (mole %): 29.8 $SiO_2$, 3.6 $P_2O_5$, 13.3 CaO, 1.3 $R_2O_3$. The content of other oxides varied within the limits (%): 8.6 – 29.0 $B_2O_3$, 0 – 15.6 ZnO, 18.0 – 36.4 $Na_2O$ (Fig. 1).

The obtained glasses were divided into several groups: clear glasses, glasses with crystalline inclusions or opacified glasses, unmelted glasses, and sinters. Based on the study of the glass formation area at temperature 1200°C (Fig. 1), certain compositions of clear and partly opacified glasses were selected for further research: 8, 9, 11, 12, 14, 15, 16. The experiments indicated that these glasses are well melted and clarified, and mold satisfactorily. They can be drawn as thin filaments, which is evidence of the wide working viscosity interval, and, consequently, good molding capacity. The glass color varied from light yellowish-green to dark green, depending on the glass composition.

To study the possibilities of synthesis of low-melting second-series glasses based on gravitation slime, the glass formation region was investigated in the slime – $B_2O_3$ – $Na_2O$ system at temperature 1100°C (Fig. 2). It follows from the obtained results that the region of clear glasses is limited by a slime content of 60 wt.% with a $B_2O_3$ content of 10 – 20%. The glasses are well clarified, have yellow-brown or honey-brown color, and exhibit liquation in the course of annealing. A dark brown opacified glass with good melting and working properties was obtained with a slime content of 70 wt.% (composition 22).

The crystallization capacity of glasses was studied by the polythermic method in a gradient furnace within the temperature range of 300 – 800°C with 1 h holding. Glasses based on phosphate ore with a high $Na_2O : B_2O_3$ ratio equal to 1.8 – 3.0 (glasses 8, 9, 11, 12) are characterized by liquation (the liquation starting temperature is 600 – 680°C). As the $Na_2O$ content in the glass composition decreases and the amount of ZnO increases, its crystallizing capacity grows. Glasses of compositions 14, 15, and 16 start crystallizing at temperatures 500 – 545°C. Using the x-ray phase analysis, it was found that the main phases isolated in the crystallization of these glasses are the low-temperature form of α-quartz, $Ca_4Al_4Fe_2O_{15}$, $Ca_3Fe_2Si_3O_{12}$, γ-$CaSiO_4$, and $Na_2CaSi_3O_8$.

Glasses based on the gravitation slime liquate at temperatures 450 – 500°C; moreover, glasses 22 ands 25 start crystallizing at temperatures 540 – 560°C. Apart from the above listed phases, glasses with the slime waste are characterized by the isolation of FeS and $Al_2TiO_5$.

The physicochemical properties of the synthesized glasses were determined using known methods [2]: the density was found by hydrostatic weighing with an accuracy ± 5 kg/m$^3$, the water resistance was determined by the molding surface method (through the weight loss) with an accuracy of ± 0.01%, the microhardness was measured on a

**TABLE 2**

| Glass | Batch composition, g | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | waste | sand | chalk | sodium polyphosphate | soda | boric acid | zinc oxide | aluminum oxide |
| Initial glass | – | 26.12 | 18.20 | 13.90 | 37.70 | 38.82 | 13.54 | 2.00 |
| Based on ore (mixture 16) | 50.60 | – | – | – | 37.18 | 38.82 | 13.54 | 1.16 |
| Based on slime (mixture 22) | 78.70 | – | – | – | 32.40 | 20.40 | – | – |

**TABLE 3**

| Glass | Density, kg/m$^3$ | Water resistance (weight loss), % | Microhardness, MPa | TCLE, $10^{-7}$ K$^{-1}$ | Dilatometric softening temperature, °C |
|---|---|---|---|---|---|
| Initial glass | 2560 | 0.12 | 2520 | 106 | 550 |
| 9 | 2600 | 0.32 | 2020 | 123 | 536 |
| 11 | 2580 | 0.35 | 2100 | 110 | 543 |
| 12 | 2585 | 0.13 | 2260 | 112 | 517 |
| 15 | 2560 | 0.08 | 2150 | 104 | 545 |
| 16 | 2565 | 0.06 | 2090 | 101 | 550 |
| 22 | 2655 | 0.04 | 2380 | 115 | 500 |
| 25 | 2640 | 0.07 | 2250 | 120 | 465 |
| 26 | 2620 | 0.05 | 2350 | 98 | 550 |
| 27 | 2615 | 0.10 | 2310 | 95 | 480 |
| 28 | 2625 | 0.14 | 2290 | 104 | 525 |

PMT-3 unit with an accuracy ± 50 MPa, and the TCLE ($\pm 10^{-7}$ K$^{-1}$) and softening temperature (± 5°C) on a DKV-5AM dilatometer.

The results of the investigation of physicochemical properties of glasses are given in Table 3. It is established that the density of most glasses based on waste is 2580 – 2655 kg/m$^3$, whereas the density of the original glass is 2560 kg/m$^3$. The introduction of phosphate wastes decreases the microhardness of glass to 2020 – 2350 MPa, compared to 2520 MPa in the original glass. Owing to that, the resulting glasses will be more amenable to treatment (grinding, polishing, cutting).

Depending on the $R_2O_3$ and $B_2O_3$ content, the TCLE of the obtained glasses varies within the range $(94 - 135) \times 10^{-7}$ K$^{-1}$. It should be noted that all glasses have a low dilatometric softening temperature (465 – 550°C); moreover, in most glasses this temperature is lower than in the original glass. Glasses based on phosphate wastes are, as a rule, resistant to water. This is especially true of glasses based on gravitation slime (compositions 22, 25, and 26; weight losses 0.04, 0.07, and 0.05%, respectively), which can be accounted for by the increased content of $Al_2O_3$, $TiO_2$, CaO and MgO introduced in the waste. The high resistance of glasses 15 and 16 (0.08 and 0.06%) is due to the ZnO content with a low ratio of $Na_2O : B_2O_3$.

The optimum glass compositions were selected subject to the condition of a decreased content of boron and sodium oxides and taking into account the investigated properties of glasses. These are glasses 12, 15, and 16 obtained on the basis of substandard phosphate ore component and glasses 22, 25, and 26 synthesized on the basis of slime waste, which all exhibit high water resistance (weight loss 0.04 – 0.13%), low softening point (465 – 550°C), and TCLE within the limits of $(98 - 120) \times 10^{-7}$ K$^{-1}$.

Since reducing agents in the form of organic compounds are introduced into the batch together with the ore processing wastes, the redox potential of the batches was quantitatively estimated by determining the chemical need of glass batches in oxygen (CNO) [3]. Furthermore, the redox potential of batches is a determining factor for the color of glass, especially glass containing ferric oxides.

**TABLE 4**

| Glass | Glass basicity modulus | CNO, mg $O_2$/100 g batch | Color |
|---|---|---|---|
| 9 | 1.20 | 397 | Brown-yellow |
| 12 | 0.98 | 388 | Yellowish-green |
| 11 | 0.90 | 384 | Greenish-yellow |
| 16 | 0.80 | 314 | Green |
| 15 | 0.73 | 345 | Dark green |
| 22 | 0.72 | 542 | Dark brown |
| 25 | 0.94 | 470 | Honey-brown |
| 26 | 0.60 | 500 | Brown |

Analysis of the results (Table 4) shows that the color of glass based on the ore is determined by the linear relationship of the CNO and the basicity modulus. With a low value of the melt basicity, the ratio $Fe^{2+} : Fe^{3+}$ determining the green color in glasses 15 and 16 increases and correlates with the smaller values of CNO. As the basicity increases, the ratio $Fe^{2+} : Fe^{3+}$ decreases, the color of glasses 9, 11, and 12 changes from yellow-green to yellow; and the CNO of these batches is higher. The CNO of glass batches 22, 25, and 26 based on gravitation slime is significantly higher, which is accounted for by the high content of ferric oxide (II) and organic impurities in the waste (Table 1). The different shades of brown color in these glasses are presumably determined only by the content of sulfoferrite.

Thus, the products of phosphate ore processing can be used as the main materials in the production of low-melting glasses in the $SiO_2 - R_2O_3 - P_2O_5 - RO - R_2O$ system. The introduction of waste will make it possible to reduce the number of batch components. Glasses of different tints of green, yellow, and brown with satisfactory service parameters have been synthesized. Based on these glasses and adding small quantities (above 100%) of oxidizing and reducing agents, opacified glasses with unique decorative effects were synthesized that simulate the texture of gem stones and can be used in the production of small decorative articles: boxes, bracelets, buttons, beads, etc.

Moreover, the use of phosphate ore processing waste will make it possible to expand the available material basis, decrease the cost of glass production, and contribute to environmental safety.

## REFERENCES

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